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(54) **Photosensitive resin composition, method for producing photosensitive resin composition, and printing plate material**

(57) A photosensitive resin composition comprising (A) a polymer as derived from its latex dispersion in water, (B) a hydrophilic photopolymerizable monomer, (C) rubber, and (D) a photopolymerization initiator, especially that as prepared by mixing (A') a latex dispersion in

water and (B) a hydrophilic photopolymerizable monomer to give a component (E), followed by kneading under heat the resulting component (E) with (C) rubber and (D) a photopolymerization initiator, can be developed with a developer not containing additives such as surfactants and alkali metal salts.

## Description

**[0001]** The present invention relates to a photosensitive resin composition for printing plates, and to a printing plate material comprising it. In particular, it relates to a water-developable, flexographic printing plate material.

**[0002]** As having the advantage of elastomer characteristics, a photosensitive resin composition that comprises, as a carrier resin component, an elastomer of, for example, chlorinated rubber, styrene-butadiene block copolymer or polyurethane and contains an ethylenically unsaturated compound and a photopolymerization initiator is useful as a flexographic printing plate material. Many proposals relating to it have been made, for example, as in US-A-2948611, US-A-3024180 and JP-B-51-043374.

**[0003]** Solid photographic resin materials for printing plates require development with halogenated hydrocarbons. It is desired to create water-developable, solid photographic resin materials for flexographic printing plates, and some proposals for them have been made.

**[0004]** In US-A-4517279, US-A-5372913 and US-A-5424172, a method has been proposed which is to prepare a photosensitive resin composition containing a hydrophilic polymer such as a carboxylated nitrile rubber and a hydrophobic polymer such as nitrile rubber. However, the composition proposed is problematic in that the aqueous developer for it must contain some additives, such as an aqueous alkaline developer or an aqueous, surfactant-containing developer, in order that the polymers in the composition could be dispersible in the developer.

**[0005]** In US-A-4275142, US-A-4272608, JP-A-51-063903, JP-A-53-010648 and JP-A-61-022339, a photosensitive resin composition comprising a carboxyl group-containing polymer has been proposed, in which the polymer is in the form of a metal salt or ammonium salt. However, the composition proposed is still problematic in that it is liquid, that its waterproofness and mechanical strength are unsatisfactory when used in printing plates, and that the aqueous developer for it must contain some additives, such as an aqueous alkaline developer or an aqueous, surfactant-containing developer.

**[0006]** For forming salt structures as in the above, another method has been proposed in US-A-5348844, US-A-5350661, US-A-5229434 and JP-B-05-006178, which comprises forming ammonium salt structures of a carboxyl group-containing polymer in the form of latex or micro-gel particles dispersed in water. They say that the composition comprising the polymeric ammonium salt is developable with water and exhibits good waterproofness when used in printing plates. However, the composition is still problematic in that its printing durability in flexography is poor, and that, since it contains intragranularly-crosslinked particles, the gel particles still remain as they are in the composition or drop away from the composition after and during its development with an aqueous developer, thereby roughening the relief edges as formed after the development. Specifically, the image reproducibility of the composition for fine relief patterns is poor.

**[0007]** The present invention addresses the problem of providing a photosensitive resin composition for flexographic printing plates with good image reproducibility, which can be developed with a developer not containing additives such as surfactants, alkali metal salts and others.

**[0008]** According to one aspect, the invention provides a precursor for providing a photosensitive resin composition, which precursor composition comprises:

a polymer latex (A') of particles of a polymer (A) dispersed in water and a hydrophilic photopolymerizable monomer (B), at least a proportion of which monomer (B) is adsorbed onto the particles of polymer (A). The precursor in accordance with the invention may additionally include (C) rubber and (D) a photopolymerization initiator.

**[0009]** According to another aspect, the invention provides a photosensitive resin composition comprising (1) a dewatered polymer latex (E) comprising particles of a polymer (A) dispersed in water and a hydrophilic photopolymerizable monomer (B), whereby at least a proportion of the said monomer (B) is adsorbed onto the polymer particles (A), (2) a rubber (C), and (3) a photopolymerization initiator (D).

**[0010]** The dewatered polymer latex (E), in such a composition, in which the polymer particles (A) have adsorbed thereon monomer (B), may be prepared by dewatering the abovementioned latex (A') of polymer particles (A) having monomer (B) adsorbed thereon either in the absence or in the presence of the rubber component (C) and initiator compound (D). In particular, dewatering may be left until all desired components of the precursor composition have been mixed.

**[0011]** In one preferred embodiment of the photosensitive composition, the polymer (A) as derived from its latex dispersion in water is dispersed in the hydrophilic photopolymerizable monomer (B).

**[0012]** The invention also provides a method for producing the photosensitive resin composition, which comprises:

mixing (A') a latex dispersion of particles of a polymer (A) in water and (B) a hydrophilic photopolymerizable monomer to give a component (E), followed by kneading, preferably under heat, the resulting component (E) with (C) rubber and (D) a photopolymerization initiator to give the composition.

**[0013]** The component (E) may be dewatered prior to kneading with components (C) and (D). Alternatively, latex component (E) may be mixed with components (C) and (D) and any other component optionally present in the composition and the composition then dewatered, either during or subsequently to kneading.

**[0014]** The invention further provides a printing plate material, which comprises:

a photosensitive layer as formed on a support by applying a photosensitive resin composition comprising (A) a polymer as derived from its latex dispersion in water containing (B) a hydrophilic photopolymerizable monomer, (C) rubber and (D) a photopolymerization initiator onto the support.

**[0015]** Preferred embodiments of the invention are now described below.

**[0016]** The component (A), the polymer present in the photosensitive resin composition of the invention, is derived from its latex dispersion in water containing monomer component (B). In the polymer latex dispersion in water, the latex polymer particles are dispersed in water owing to their electric repulsion, and they are electrically charged in water through the ionization of emulsifier, protective colloid, polymer and others therein and through the adsorption of the particles of those components to each other. The polymer (A) indicates the latex polymer particles being dispersed in water in that condition.

**[0017]** The polymer as derived from its latex dispersion in water has the property of forming a continuous film after water around it evaporates away. Even though derived from its latex dispersion in water, a polymer having a high intragranular crosslinking density could hardly form a continuous film. Therefore, in the invention, it is desirable that the polymer particles are not intragranularly crosslinked or, even though being intragranularly crosslinked to some degree, they have a low intragranular crosslinking density.

**[0018]** More specifically, polymer components which may be used are aqueous dispersions of latex polymers such as polybutadiene latex, natural rubber latex, styrene-butadiene copolymer latex, acrylonitrile-butadiene copolymer latex, polychloroprene latex, polyisoprene latex, polyurethane latex, methyl methacrylate-butadiene copolymer latex, vinylpyridine polymer latex, butyl polymer latex, thickol polymer latex, acrylate polymer latex, as well as those of latex copolymers of those monomers as copolymerized with any other monomer component such as acrylic acid and methacrylic acid. Of those, preferred are aqueous dispersions of latex polymers having a butadiene or isoprene skeleton in the molecular chain, in view of the hardness of the cured polymers. Thus, more preferred are polybutadiene latex, styrene-butadiene copolymer latex, acrylonitrile-butadiene copolymer latex, methyl methacrylate-butadiene copolymer latex and polyisoprene latex.

**[0019]** The component (B) for use in the invention acts to prevent the aggregation of the component (A). Specifically, a film of the component (B) is formed around the surfaces of the particles of the component (A), whereby the aggregation of the particles of the component (A) is retarded.

**[0020]** As the component (B) having an ability to prevent the aggregation of the component (A), herein used is a hydrophilic monomer. The hydrophilic monomer for use in the invention is meant to include compounds having an ethylenically unsaturated bond and having a molecular structure conferring hydrophilic properties as exemplified below.

**[0021]** Specific molecular structures which the hydrophilic monomer for use in the invention may have are a polyalkylene glycol structure, a carboxyl group-containing structure, a hydroxyl group-containing structure and a phosphoric acid group-containing structure.

**[0022]** Specific examples of the polyalkylene glycol-containing monomers are polyethylene glycol di(meth)acrylates such as diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate and tetraethylene glycol di(meth)acrylate; polypropylene glycol di(meth)acrylates such as dipropylene glycol dimethacrylate, tripropylene glycol di(meth)acrylate and tetrapropylene glycol di(meth)acrylate; phenoxyethylene glycol (meth)acrylates such as phenoxydiethylene glycol (meth)acrylate, phenoxytriethylene glycol (meth)acrylate, phenoxytetraethylene glycol (meth)acrylate and phenoxy-pentaethylene glycol (meth)acrylate; phenoxypropylene glycol (meth)acrylates such as phenoxydipropylene glycol (meth)acrylate, phenoxytripropylene glycol (meth)acrylate and phenoxytetrapropylene glycol (meth)acrylate; as well as other monomers of, for example, polyethylene glycol-polypropylene glycol di(meth)acrylate, cresylpolyethylene glycol (meth)acrylate and nonylphenoxyethylene glycol (meth)acrylate.

**[0023]** The hydroxyl group-containing monomers include, for example, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl(meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate,  $\beta$ -hydroxy- $\beta'$ -(meth)acryloyloxyethyl phthalate and 2-hydroxy-3-acryloyloxypropyl (meth)acrylate.

**[0024]** The carboxyl group-containing monomers include, for example,  $\beta$ -carboxyethyl (meth)acrylate, mono(meth)acryloyloxyethyl succinate and monohydroxyethyl phthalate (meth)acrylate.

**[0025]** The phosphoric acid group-containing monomers include, for example, 2-(meth)acryloyloxy acid phosphate, tris(acryloyloxy) phosphate, caprolactone-modified 2-(meth)acryloyloxyethyl acid phosphate, (meth)acryloyloxyethyl acid phosphate and diphenyl-2-(meth)acryloyloxyethyl phosphate. The terminology, "(meth)acrylate" as referred to herein means "methacrylate" and "acrylate" as respective examples.

**[0026]** As in the above, the polyalkylene glycol-containing monomers, the carboxyl group-containing monomers, the

hydroxyl group-containing monomers and the phosphoric acid group-containing monomers are preferred, as their ability to prevent the aggregation of the component (A) is high.

**[0027]** Preferably, the amount of the component (B) present in the composition is from 10 to 200 parts by weight, relative to 100 parts by weight of the component (A) therein. The composition in which the amount of the component (B) is 10 parts by weight or more is preferred, as having sufficient crosslinking density and good image reproducibility. The composition in which the amount of the component (B) is not more than 200 parts by weight is also preferred, since the relief patterns formed from it are tough and since the component (B) therein is not separated during storage.

**[0028]** If desired, the composition of the invention may contain a hydrophobic monomer not interfering with the effect of the invention. As a rule, hydrophobic monomers do not have a polar functional group.

**[0029]** Specifically, hydrophobic monomers that may be in the composition include alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, isoamyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate and stearyl (meth)acrylate; cycloalkyl (meth)acrylates such as cyclohexyl (meth)acrylate; halogenated alkyl (meth)acrylates such as chloroethyl (meth)acrylate and chloropropyl (meth)acrylate; alkoxyalkyl (meth)acrylates such as methoxyethyl (meth)acrylate, ethoxyethyl (meth)acrylate and butoxyethyl (meth)acrylate; phenoxyalkyl (meth)acrylates such as phenoxyethyl (meth)acrylate and nonylphenoxyethyl (meth)acrylate.

**[0030]** The amount of the hydrophobic monomer, if in the composition, is preferably not larger than 200 parts by weight, relative to 100 parts by weight of the component (A) therein. If it is larger than 200 parts by weight, the water developability of the composition will lower and the composition could not form good relief patterns.

**[0031]** The rubber component (C) may be any ordinary rubber or elastomer well known in the art. Specifically, it includes butadiene rubber, nitrile rubber, acrylic rubber, epichlorohydrin rubber, urethane rubber, isoprene rubber, styrene-isoprene rubber, styrene-butadiene rubber, ethylenepropylene copolymer and polyethylene chloride. If not containing the rubber component, the photosensitive resin composition could not have increased rubber elasticity and could not exhibit aqueous ink resistance.

**[0032]** The amount of the component (C) in the composition is preferably from 20 to 300 parts by weight, relative to 100 parts by weight of the component (A) therein. The composition in which the amount of the component (C) is 20 parts by weight or more is preferred, since the printing plate comprising a layer of the composition has good water-proofness and since the resiliency of the printing plate is lowered so as not to worsen the printing capabilities thereof. The composition in which the amount of the component (C) is not more than 300 parts by weight is also preferred, since the composition could have good water developability.

**[0033]** Also preferably, the ratio by weight of the total of the component (A) and the component (B) to the component (C) is at least 1. The composition having the ratio of at least 1 is preferred, since its water development speed is high and the composition is especially practicable.

**[0034]** The photosensitive resin composition of the invention contains a photopolymerization initiator as the component (D). The photopolymerization initiator may be any and every one having an ability to initiate photopolymerization of polymerizable carbon-carbon unsaturated groups. Above all, preferred are those capable of absorbing light to give a radical through autolysis or hydrogen desorption. For example, herein usable are benzoin alkyl ethers, benzophenones, anthraquinones, benzils, acetophenones and diacetyls. Preferably, the amount of the photopolymerization initiator to be in the composition is from 0.1 to 50 parts by weight relative to 100 parts by weight of the component (A) therein.

**[0035]** The composition in which the amount of the photopolymerization initiator is 0.1 parts by weight or more is preferred, since the polymerization initiation efficiency of the composition is not lowered and the image reproducibility of the composition is good. The composition in which the amount of the photopolymerization initiator is not more than 50 parts by weight is also preferred, since the sensitivity of the composition is not too high and the exposure time for the composition is easy to control.

**[0036]** The photosensitive resin composition of the invention may optionally contain a plasticizer. The plasticizer is not specifically defined, so far as it has the property of softening printing plate materials. Preferably, however, the plasticizer for use in the invention shall have good compatibility with the polymer components (A) and (C). More preferred as the plasticizer are polyene compounds or ester bond-containing compounds that are liquid at room temperature. The polyene compounds that are liquid at room temperature include liquid polybutadiene and polyisoprene, and their terminal-modified or side chain-modified maleates and epoxidates. The ester bond-containing compounds include phthalates, phosphates, sebacates, adipates and polyesters having a molecular weight of from 1,000 to 3,000.

**[0037]** The amount of the plasticizer, if in the composition, is preferably not larger than 100 parts by weight, relative to 100 parts by weight of the component (A) therein, in order that the solid plate comprising a layer of the composition could have satisfactory mechanical strength before it is subjected to photo-crosslinking treatment.

**[0038]** In order to enhance the thermal stability of the photosensitive resin composition of the invention, any known polymerization inhibitor may be added to the composition. As the polymerization inhibitor to be added to the composition, preferred are phenols, hydroquinones and catechols. The amount of the polymerization inhibitor to be in the

composition is generally from 0.001 to 5% by weight of the total weight of the composition.

[0039] As other additives, the composition may further contain any of dyes, pigments, surfactants, defoaming agents, UV absorbents and flavors.

[0040] In the photosensitive resin composition of the invention, it is desirable that the polymer (A) as derived from its latex dispersion in water is dispersed in the component (B), hydrophilic monomer. In that condition, the polymer particles (A) do not aggregate in the composition.

[0041] The morphology of the photosensitive resin composition can be observed with an electron microscope. Briefly, the composition is photo-cured through exposure to UV rays, and the cured block is sliced into thin sections having a thickness of about 200  $\mu\text{m}$ . If desired, the sections are stained with osmate or phosphorus-tungsten lake, and observed with a transmission electron microscope to know the morphology of the composition.

[0042] In the method for producing the photosensitive resin composition of the invention, it is desirable to mix the component (A'), latex dispersion in water and the component (B) to prepare the component (E). In this stage, the particles of the component (A) adsorb the component (B), and do not aggregate.

[0043] The component (E) is kneaded with the component (C) and the component (D) in a kneading system under heat, with water being removed from the resulting mixture, to produce the photosensitive resin composition of the invention.

[0044] Alternatively, the component (E) is previously dewatered in a drying system, and then kneaded under heat with the component (C) and the component (D) in a kneading system such as an extruder or a kneader to produce the photosensitive resin composition. In view of its producibility, preferred is the method comprising the predrying step of dewatering the component (E) in a drying system.

[0045] The kneading system is not specifically defined. For example, employable are a double-screw extruder, a single-screw extruder, a kneader or a Banbury mixer.

[0046] The photosensitive resin composition is applied onto a support coated with an adhesive, through melt extrusion with an extruder, and a cover film coated with a sticking preventing layer is contacted with the photosensitive layer thus formed on the support to produce a photosensitive resin plate for printing plates. Alternatively, the photosensitive resin composition may be sandwiched between a support and a cover film such as those noted above, and pressed under heat until the photosensitive layer thus formed therebetween could have a predetermined thickness. In that manner, also produced is a photosensitive resin plate for printing plates. For the support, preferably used are metal sheets of, for example, steel, stainless steel and aluminium, or plastic sheets of polyesters and others, or synthetic rubber sheets of styrene-butadiene rubber and others. Preferably, the thickness of the photosensitive layer formed is from 0.01 to 10mm. If the thickness is smaller than 0.01mm, when such a thin photosensitive layer is patterned, the relief depth will be unsatisfactory for flexographic printing plates. If, on the other hand, the thickness of the photosensitive layer is larger than 10mm, the plate material is too heavy and will lose its practical application for printing plates.

[0047] To form a relief image for printing on the photosensitive resin plate thus produced in the manner mentioned above, for example, the plate is first exposed to UV rays from a light source for UV rays having a wavelength of from 300 to 400nm, such as a high-pressure mercury vapor lamp, an ultra-highpressure mercury vapor lamp, a metal halide lamp, a xenon lamp, a carbon arc lamp or a chemical lamp, with the light source being positioned at the support side of the plate; then the cover film is peeled off from the thus-exposed plate, and a negative or positive original image film is contacted with the photosensitive layer; and thereafter the photosensitive layer of the plate is again exposed to UV rays via the image film as contacted with it, whereby the layer is photo-cured through photopolymerization.

[0048] After thus being processed, the plate is developed and rinsed with water in a spray-type developing device or a brush-type rinsing device to remove the non-polymerized part from the plate. In that manner, a relief image is formed on the support of the plate. The plate with the relief image is dried and then processed with actinic rays to be a printing plate.

[0049] The photosensitive resin composition of the invention is most suitable to flexographic printing plates, but may also be used for relief printing plates, lithographic printing plates, intaglio printing plates, mimeographic sheets and photoresists.

[0050] Embodiments of the invention will now be described in more detail with reference to the following Examples and photomicrograph, which shows a TEM (transmission electron microscope) image (x40,000) of an exposed sample of the photosensitive resin composition of the invention as prepared in Example 7,

#### Synthesis Example 1:

[0051] As starting materials, 100 parts by weight of water, 0.2 parts by weight of sodium dodecylbenzenesulfonate, 3 parts by weight of polyoxyethylene nonylphenyl ether, 0.3 parts by weight of potassium persulfate, 0.2 parts by weight of t-dodecylmercaptan, 29 parts by weight of methyl methacrylate, 1 part by weight of methacrylic acid, and 70 parts by weight of butadiene were reacted at 50°C for 20 hours to prepare a latex rubber dispersion in water, which had a number-average particle size of 140nm, a glass transition temperature of 52°C and a solid concentration of 50.5%.

## Synthesis Example 2:

[0052] As starting materials, 65 parts by weight of water, 1.3 parts by weight of disproportionated potassium rhodinate, 1.7 parts by weight of potassium oleate, 1.5 parts by weight of sodium alkylsulfonate, 0.05 parts by weight of t-dodecylmercaptan, 0.1 parts by weight of paramenthane hydroperoxide, 0.003 parts by weight of iron sulfate, 0.006 parts by weight of sodium ethylenediaminetetraacetate, 0.05 parts by weight of sodium formaldehyde sulfoxylate, 1.2 parts by weight of potassium sulfate and 100 parts by weight of butadiene were reacted for low-temperature polymerization at a polymerization temperature of 5°C. The degree of polymerization conversion was about 60%. A latex rubber dispersion in water was obtained, which had a number-average particle size of 350nm and a solid concentration of 55%.

## Synthesis Example 3:

[0053] The same process as in Synthesis Example 1 was repeated, except that 50 parts by weight of methyl methacrylate and 50 parts by weight of butadiene were used, to prepare a latex rubber dispersion in water, which had a number-average particle size of 160nm, a glass transition temperature of -27°C and a solid concentration of 50.0%.

## Synthesis Example 4:

[0054] The same process as in Synthesis Example 1 was repeated, except that 24 parts by weight of methyl methacrylate, 1 part by weight of acrylic acid in place of the methacrylic acid, and 75 parts by weight of butadiene were used, to prepare a latex rubber dispersion in water, which had a number-average particle size of 180nm and a solid concentration of 50.5%.

## Example 1:

[0055] 33.6 parts by weight (17 parts by weight in terms of the solids content) of the latex dispersion in water as prepared in Synthesis Example 1 and 14.5 parts by weight (8 parts by weight of the solids content) of the latex dispersion in water as prepared in Synthesis Example 2, both containing the component (A), were previously mixed with 16 parts by weight of phenoxypolyethylene glycol acrylate and 14 parts by weight of a polycondensate of glycerin polyetherpolyol, succinic anhydride and 2-hydroxyethyl acrylate, the two constituting the component (B), and then dewatered in a drier at 120°C for 2 hours to prepare a mixture serving as the component (E). On the other hand, 20 parts by weight of polybutadiene rubber (Nipol 1220L from Nippon Zeon) and 20 parts by weight of nitrile rubber (Nipol 1042 from Nippon Zeon), the two constituting the component (C), were kneaded in a 200-ml laboratory kneader mill (from Toshin) at 140°C for 10 minutes. After this, the component (E) was put into the laboratory kneader mill, in which the components were further kneaded for 10 minutes. Next, 1 part by weight of a photopolymerization initiator component (D), 2 parts by weight of dioctyl phthalate serving as a plasticizer, and 0.1 parts by weight of hydroquinone monomethyl ether serving as a polymerization inhibitor were put into the mill, in which all were still further kneaded for 5 minutes to give a photosensitive resin composition.

[0056] The resulting photosensitive resin composition was sandwiched between a substrate (support) of a 125 µm-thick polyethylene terephthalate film coated with a polyester-type adhesive, and a cover film of a 100 µm-thick polyethylene terephthalate film coated with a polyvinyl alcohol-based polymer, and so pressed with a presser heated at 150°C that the layer of the photosensitive resin composition had a thickness of 3mm. In that manner, obtained was a photosensitive resin printing plate.

[0057] The photosensitive resin printing plate was exposed to light in an exposing device having fifteen 20-W chemical lamps disposed therein in parallel. Briefly, the plate was so set in the device that its support faced the lamps via a space of 15cm therebetween, and was exposed to the light from the lamps for 1 minute. Next, the cover film was peeled off from the plate, and a negative film for image reproducibility evaluation (having 150 lines with 3% dots, independent dots of 200 µm in diameter and fine lines of 50 µm in width) was airtightly contacted with the photosensitive resin layer formed on the plate. In that condition, the plate was again exposed to the same chemical lamps for 10 minutes. After being exposed in that manner, the plate was developed in a brush-type washer filled with water (liquid temperature; 40°C). Having been thus washed for 9 minutes, the plate had a relief image of 700 µm in depth. This was then dewatered in a drier at 60°C. Next, this was subjected to post-exposure to actinic rays to form a printing plate. The image formed on the printing plate was visually checked. It was found that the image formed on the printing plate was faithful to the original image of the negative film.

[0058] The printing plate had a degree of resiliency of 32%, a degree of swelling with water of 1.8%, and a Shore A hardness of 57.

[0059] The printing plate was installed in a flexographic printing machine in which was used an aqueous ink, and subjected to a printing test to duplicate 100,000 copies. The copies were all good. Briefly, the copies duplicated were

compared with the original image in the negative film, and checked as to whether or not they were faithful to the original image. Those having a faithful image were judged good.

[0060] The composition for the printing plate is shown in Table 1. The developing speed, the image reproducibility, the degree of swelling with water, the Shore A hardness, the degree of resiliency, and the flexographic printing test data are in Table 2.

Table 1

	Component (A)	Component (B)	Component (C)	Component (D)	Others
Example 1	Synthesis Example 1: 17 Synthesis Example 2: 8	Monomer 1: 16 Monomer 2: 14	BR: 20 NBR1: 20	Initiator: 1	MEHQ: 0.1
Example 2	Synthesis Example 1: 22	Monomer 1: 34 Monomer 2: 5	BR: 10 NBR1: 24	Initiator: 1	MEHQ: 0.1
Example 3	Synthesis Example 3: 22	Monomer 1: 20 Monomer 3: 18	NBR2: 20 NBR3: 20	Initiator: 1	MEHQ: 0.1
Example 4	Synthesis Example 1: 17 Synthesis Example 2: 8	Monomer 1: 16 Monomer 2: 14	BR: 20 NBR3: 20	Initiator: 1	MEHQ: 0.1
Example 5	Synthesis Example 2: 8 Synthesis Example 4: 17	Monomer 1: 17 Monomer 2: 16	BR: 12 NBR2: 36 NBR3: 4	Initiator: 1	MEHQ: 0.1
Example 6	Synthesis Example 1: 17 Synthesis Example 2: 8	Monomer 1: 10 Monomer 2: 10	BR: 13 NBR2: 25 NBR3: 13	Initiator: 1	MEHQ: 0.1
Example 7	Synthesis Example 1: 17 Synthesis Example 2: 8	Monomer 1: 16 Monomer 2: 14	BR: 12 NBR2: 24 NBR3: 4	Initiator: 1	MEHQ: 0.1
Comparative Example 1	None	Monomer 1: 16 Monomer 2: 14	BR: 20 NBR1: 20	Initiator: 1	MEHQ: 0.1
Comparative Example 2	Synthesis Example 1: 17 Synthesis Example 2: 8	None	BR: 20 NBR1: 20	Initiator: 1	MEHQ: 0.1 Monomer 4: 30
Comparative Example 3	Synthesis Example 1: 17 Synthesis Example 2: 8	Monomer 1: 16 Monomer 2: 14	BR: 20 NBR1: 20	Initiator: 1	MEHQ: 0.1

[0061] The amounts are all by weight, but the amount of the monomers for the component (B) is in terms of the solids content by weight.

[0062] Abbreviations are as follows:

BR	Butadiene rubber (Nipol 1220L from Nippon Zeon)
NBR1	Nitrile rubber (Nipol 1042 from Nippon Zeon)
NBR2	Partially crosslinked nitrile rubber (Nipol DN214 from Nippon Zeon)
NBR3	Carboxylated NBR (Nipol 1072 from Nippon Zeon)
Monomer 1	Phenoxydiethylene glycol acrylate
Monomer 2	Polycondensate of glycerin polyether polyol, succinic anhydride and 2-hydroxyethyl acrylate
Monomer 3	Nonylphenyltetraethylene glycol methacrylate
Monomer 4	Lauryl acrylate
Initiator	Benzyl dimethyl ketal
MEHQ	Hydroquinone monomethyl ether

Examples 2 to 7, and Comparative Examples 1 and 2:

[0063] Using the compositions indicated in Table 1, printing plate materials were produced in the same manner as in Example 1. These were exposed and developed also in the same manner as in Example 1 to have a relief depth of about 700  $\mu\text{m}$ . As in Example 1, the developing speed, the image reproducibility, the degree of swelling with water, the Shore A hardness, the degree of resiliency, and the flexographic printing test data are shown in Table 2.

Comparative Example 3:

[0064] The same components as in Example 1 were used to prepare a photosensitive resin composition. However, the method for preparing it differs from that in Example 1, and is as follows:

A laboratory kneader mill (from Toshin) was heated at 140°C. The component (C) was put into this, and kneaded for 10 minutes. The latex dispersion (A') prepared in Synthesis Example 1 and serving as the component (A') was previously dewatered in a drier, then put into the mill, and kneaded therein. The latex dispersion (A') prepared in Synthesis Example 2 and serving as the component (A') was also dewatered, put into the mill and kneaded therein in the same manner. Next, the two monomers serving as the component (B) were pre-mixed, and the resulting liquid mixture was put into the mill and kneaded. In the initial stage of the process, the components slipped in the mill and could not be kneaded well, but, after a while, they were well kneaded. Last, the component (D) and the additive were added to the mill and further kneaded to prepare a photosensitive resin composition.

[0065] Using the composition, a photosensitive resin plate was produced in the same manner as in Example 1. The plate was exposed and developed also in the same manner as in Example 1 to be a printing plate.

[0066] After being developed, the surface of the printing plate was observed. Many gel particles existed on the surface of the plate, though washed through development. It is believed that the latex polymer as separated from its aqueous dispersion would aggregate to give the gels since it was dried prior to being mixed with the other components. In the relief pattern formed, the gel particles partly dropped off, and the relief pattern was not faithful to the original image in the negative film.



Table 2

	Developing Speed ( $\mu\text{m}/\text{min}$ )	Hardness (Shore A)	Degree of Resiliency (%)	Image Reproducibility	Degree of Swelling with Water (%)	Printability
Example 1	78	57	32	Good	1.8	Good
Example 2	197	51	38	Good	2.6	Good
Example 3	74	32	37	Good	1.0	Good
Example 4	73	50	32	Good	1.5	Good
Example 5	223	56	30	Good	1.9	Good
Example 6	7	46	33	Good	1.4	Good
Example 7	105	57	33	Good	1.7	Good
Comparative Example 1	Poorly kneaded.					
Comparative Example 2	Water development impossible.					
Comparative Example 3	Gel particles existed, relief reproducibility not good.					

Hardness:

[0067] Measured at room temperature (25°C).

Degree of resiliency:

**[0068]** An iron ball weighing 5.8g was dropped down onto the printing plate. The ratio by percentage of the rebounded height to the dropping height indicates the degree of resiliency.

Image Reproducibility:

**[0069]**

Good: Faithful to the original image of the negative film.  
 Poor: Not faithful to the original image of the negative film.

Degree of Swelling in Water:

**[0070]** Weight increase after immersed in water for 24 hours. Printability:

Good: After the printing test, the relief edges and the surface of the printing plate did not change.  
 Poor: After the printing test, the relief edges of the printing plate were partly broken and the surface thereof was roughened.

Morphology Observation:

**[0071]** The photosensitive resin-coated printing plate material having been produced in Example 7 was exposed to the same chemical lamps as those used in Example 1. First, the printing plate was exposed for 5 minutes at the support side, then the cover film was peeled off, and the plate was again exposed for 10 minutes at the side of the resin layer. The thus-exposed resin layer was sliced into sections having thickness of about 200nm, according to a method of freezing and slicing ultra-thin film sections. The sections were observed with a transmission electron microscope (H-600 Model made by Hitachi, Ltd.) to identify the morphology of the cured resin composition. Fig.1 shows the TEM image (x 40,000) of the exposed resin composition.

**[0072]** As seen in the TEM image, the polymer particles of the component (A) derived from the latex dispersion in water (these particles are seen as spheres of about 200 nm in size) are dispersed in the hydrophilic monomer of the component (B) (this is seen as the white background area).

**[0073]** In the resin composition, the structure moiety with the component (A) being dispersed in the component (B) is hydrophilic. As having the hydrophilic structure moiety, the resin composition could be developed with water.

## Claims

1. A photosensitive resin composition comprising (1) a dewatered polymer latex (E) comprising particles of a polymer (A) dispersed in water and a hydrophilic photopolymerizable monomer (B), whereby at least a proportion of the said monomer (B) is adsorbed onto the polymer particles (A), (2) a rubber (C), and (3) a photopolymerization initiator (D).
2. A photosensitive resin composition according to claim 1, wherein the amount of the monomer component (B) is from 10 and 200 parts by weight, that of the rubber component (C) is from 20 to 300 parts by weight and that of the initiator component (D) is from 0.1 to 50 parts by weight, each relative to 100 parts by weight of the polymer component (A).
3. A photosensitive resin composition according to claim 1 or claim 2, wherein the ratio by weight of the total of the polymer component (A) and the monomer component (B) to the component (C) is at least 1:1.
4. A photosensitive resin composition according to any preceding claim, wherein the polymer component (A) has a butadiene or isoprene skeleton in its molecular chain.
5. A photosensitive resin composition according to claim 4, wherein the polymer component (A) is at least one polymer or copolymer selected from polybutadiene, styrene-butadiene copolymer, acrylonitrile-butadiene copolymer, methyl methacrylate-butadiene copolymer, polyisoprene, and copolymers of these with other polymerizable monomers.

6. A photosensitive resin composition according to any preceding claim, wherein the hydrophilic photopolymerizable monomer component (B) is at least one monomer selected from a monomer having polyalkylene glycol in its molecular structure, a monomer having carboxyl groups, a monomer having hydroxyl groups and a monomer having phosphoric acid groups.
7. A photosensitive resin composition according to any preceding claim, wherein the polymer component (A) is dispersed in the hydrophilic photopolymerizable monomer component (B) morphologically.
8. A method for producing a photosensitive resin composition, which comprises mixing (A) a latex dispersion of particles of a polymer (A) in water and (B) a hydrophilic photopolymerizable monomer to give a component (E), followed by kneading the resulting component (E) with (C) rubber and (D) a photopolymerization initiator.
9. A method according to claim 8, wherein the component (E) is dewatered, and the resulting dry component (D) is kneaded under heat with the component (C) and the component (D).
10. A method according to claim 9, wherein dewatering of component (E) is carried out during or subsequently to kneading thereof with components (C) and (D), whereby the mixture of components (E), (C) and (D) is dewatered.
11. A printing plate material comprising a photosensitive layer as formed on a support by applying a photosensitive resin composition of any one of claims 1 to 7 onto the support.
12. A printing plate material comprising a photosensitive layer as formed on a support by applying the photosensitive resin composition having been prepared by the production method of any one of claims 8 to 10, onto the support.
13. A precursor composition for providing a photosensitive composition, which precursor composition comprises a polymer latex (A') comprising particles of a polymer (A) dispersed in water and a hydrophilic photopolymerizable monomer (B), at least a proportion of which monomer (B) is adsorbed onto the particles of polymer (A).
14. A precursor composition according to claim 13, which additionally includes (C) a rubber and (D) a photopolymerizable initiator.





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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 30 5031

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>11 October 1999</b>	Examiner <b>Heywood, C</b>
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

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